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The ozonolysis of primary aliphatic amines in single and multicomponent fine particles

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Abstract

The oxidative processing by ozone of the particulate amines octadecylamine (ODA) and hexadecylamine (HDA) is reported. Ozonolysis of these amines resulted in strong NO_2^- and NO_3^- ion signals that increased with ozone exposure as monitored by photoelectron resonance capture ionization aerosol mass spectrometry. These products suggest a mechanism of progressive oxidation of the particulate amines to nitro alkanes. Additionally, a strong ion signal at 125 *m/z* is assigned to the ion $NO_3^-(HNO_3)$. For ozonized mixed particles containing ODA or HDA + oleic acid (OL), with $p_{O3} \geq 3 \times 10^{-7}$ atm, imine, secondary amide, and tertiary amide products were measured. These products most likely arise from reactions of amines with aldehydes (for imines) and stabilized Criegee intermediates (SCI) or secondary ozonides (for amides) from the fatty acid. The routes to amides via SCI and/or secondary ozonides was shown to be more important than comparable amide forming reactions between amines and organic acids, using azelaic acid as a test compound. Finally, direct evidence is provided for the formation of a surface barrier in the ODA + OL reaction system that resulted in the retention of OL at high ozone exposures (up to 10^{-3} atm for 17 s). This effect was not observed in HDA + OL or single component OL particles, suggesting that it may be a species-specific surfactant effect from an in situ generated amide or imine. Implications to tropospheric chemistry, including particle bound amines as sources of oxidized gas phase nitrogen species (e.g. NO_2, NO_3), formation of nitrogen enriched HULIS via ozonolysis of amines and source apportionment are discussed.

1 Introduction

Amines, including aliphatic amines, represent an important contributor to organic nitrogen in the atmosphere and stem from both anthropogenic and biogenic emissions. Animal husbandry is probably the most important anthropogenic emission source of amines into the troposphere (Rabaud et al., 2003; Filipy et al., 2006), with Schade and

Crutzen (Schade and Crutzen 1995) having estimated contributions up to 108±30 and 24±15 Gg N y^{-1} for trimethylamine and methylamine to the atmosphere, respectively; albeit this is still 2–3 orders of magnitude lower than ammonia (23.3 Tg N y^{-1}). Agriculture (Beddows et al., 2004) and biomass burning (Mace et al., 2003; Decesari et al., 2006) may also be important sources of amines to the troposphere. Other anthropogenic sources of amine or amine-derived nitrogen to the troposphere include vehicular emissions (Angelino et al., 2001), industrial processes, and cooking (Rogge et al., 1991; Schauer et al., 1999). In the marine troposphere organic amine nitrogen, including amino acids, may enter the troposphere via a bubble bursting mechanism at the air-sea interface (Milne and Zika, 1993). Other biogenic sources of organic nitrogen, including amines, are addressed in the assessment provided by Neff and coworkers (Neff et al., 2002).

There is growing evidence that organic nitrogen, including amines and amine-derived compounds, may form a substantial fraction of the organic aerosol load as evidenced in recent field studies in remote (Mäkelä et al., 2001; Beddows et al., 2004), urban (Angelino et al., 2001; McGregor and Anastasio, 2001; Tan et al., 2002; Simoneit et al., 2003), and agricultural (Angelino et al., 2001; McGregor and Anastasio, 2001) regions, and in regions near extensive biomass burning (Mace et al., 2003; Simoneit et al., 2003; Decesari et al., 2006).

Gas phase aliphatic amines may play a role in secondary aerosol formation (Angelino et al., 2001; Murphy et al., 2007) via photooxidation and gas-to-particle conversion. Recent field observations have positively correlated episodic aerosol formation events with elevated concentrations of atmospheric amines. For example, Tan et al. have found in one episodic event of elevated $PM_{2.5}$ in an urban environment that organic amines were evident in all the particulate (Tan et al., 2002). Similarly, in remote boreal forest studies, Mäkelä and coworkers (Mäkelä et al., 2001) found a strong positive correlation between new particle formation events and the concentration of dimethylammonium (the ionic component of dimethylamine). This amine-derived species had more than 30-fold greater concentration during particle formation events

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as opposed to non-event concentrations for accumulation mode particles. In light of these recent findings, we believe that the role of amines and other forms of organic nitrogen in new particle formation events merits further investigation.

There is a need to develop a better model of the tropospheric chemical processing of amines and amine nitrogen, including understanding its incorporation into high molecular weight matter, such as humic like substances (i.e. HULIS) (Likens and Galloway, 1983; Decesari et al., 2006) found in aerosols and hydrometeors. Answering questions about how nitrogen is incorporated into HULIS and its subsequent atmospheric processing is important in developing a better understanding of the aging of fine particulate matter in the troposphere. This processing may have implications on the cloud condensation nuclei ability of these particles, affecting global climate through indirect aerosol effects (Lohmann and Feichter, 2005) through the formation of more polar, water soluble compounds in aerosols. Moreover, developing a more comprehensive model of how amines and other classes of organic nitrogen are processed in atmospheric particles will give us a better description of the deposition of nitrogen, and most broadly, better elucidate the role of organic nitrogen in the global nitrogen cycle – an area of high uncertainty and great concern (Neff et al., 2002; Galloway et al., 2004).

Herein, we report on the heterogeneous ozonolysis of two long-chain, primary, aliphatic amines (octadecylamine, ODA; and hexadecylamine, HDA) in single component and mixed fine mode particles. These high molecular weight, low-volatility amines were chosen as model systems to minimize particle-to-gas phase partitioning, such that we could study their condensed phase reactivity in the aerosol. The second constituent in the two-component particles is either oleic acid (i.e. *cis*-9-octadecenoic acid, OL) or dioctyl sebacate (i.e. *bis*(2-ethylhexyl) sebacate, DOS). OL is a logical constituent for these particles in that it, and other fatty acids, are ubiquitous in the troposphere, forming coatings on continental aerosols (Tervahattu et al., 2005) and marine particulate matter (Mochida et al., 2002; Tervahattu and Juhanoja, 2002; Kawamura et al., 2003), and are present in urban atmospheres as cooking (Rogge et al., 1991; Schauer et al., 2002; Robinson et al., 2006; Zhao et al., 2007) and combustion (Wang et al., 2006) emissions. Moreover, OL was chosen as a constituent for the mixed particles studies to investigate the reactivity of the products of ozonolysis of a common unsaturated fatty acid with the amines. As of late, a great deal of effort has gone into understanding the secondary chemistry resulting from the ozonolysis of unsaturated fatty acids (Hearn et al., 2005; Hung et al., 2005; Zahardis et al., 2005; Ziemann, 2005; Gross et al., 2006; Reynolds et al., 2006) and OL has emerged as a model compound for describing the heterogeneous ozonolysis of particulate rich in fatty acid content (for example, see review by Zahardis and Petrucci, 2007). The products of this secondary chemistry generally stem from the high reactivity of stabilized Criegee intermediates (SCI) and include high molecular weight, peroxidic oligomers (Hearn et al., 2005; Hung et al., 2005; Katrib et al., 2005; Ziemann, 2005; Gross et al., 2006; Reynolds et al., 2006; Zahardis et al., 2006a; Hung and Ariya, 2007). These types of products may have a role in the experimentally observed increase in hygroscopicity and CCN activation of fine organic particles with ozonation (Broekhuizen et al., 2004; King et al., 2004; Hung and Ariya, 2007; Shilling et al., 2007). Conversely, DOS and similar high molecular weight esters (i.e. dioctyl adipate) are common constituents in studies of organic particles (Ziemann, 2005; Mochida et al., 2006) that are not a source of SCI and inert to ozone (Mochida et al., 2006); hence, DOS serves as an excellent negative control for comparison to the studies of ozonized mixed particles of amines with OL.

Two specific goals of this work were to: a) identify chemical classes that may act as particle bound nitrogen sinks and that are representative of oxidatively stressed particulate matter; and b) compare the products formed from heterogeneous ozonolysis of particle bound alkyl amines with gas phase and solution chemistries. From this we hope to begin to better describe the atmospheric aging process of particles rich in organic nitrogen; identify chemical classes that may act potential molecular markers; and elucidate possible routes to nitrogen-rich HULIS formation.

2 Experimental method

In this work we describe flow reactor based experiments employing photoelectron resonance capture ionization aerosol mass spectrometry (PERCI AMS), described in detail elsewhere (LaFranchi and Petrucci, 2006). Briefly, molecular ionization by capture of low energy photoelectrons is a soft process that affords minimal fragmentation of the oxidized products with a high sensitivity for many oxygenated classes (LaFranchi and Petrucci, 2004; LaFranchi and Petrucci, 2006) allowing for relatively straight-forward mass spectral interpretation and subsequent product identification and mechanism development. Two modes of ionization have been described with near 0 eV photoelectron attachment to organic molecules, namely associative (or non-dissociative) and dissociative electron attachment (AEA and DEA respectively). In AEA a low energy photoelectron attaches to the molecule without any fragmentation of the analyte in the ionization process; whereas, DEA results in the loss of an atomic or molecular fragment concomitant to ionization of the analyte (LaFranchi et al., 2004; Zahardis et al., 2005, 2006a, c).

Polydisperse aerosols were generated using a glass, concentric pneumatic nebuliser (J. E. Meinhard Associates, Santa Ana, CA) and the solvent (100% ethanol) was removed by passing the particle beam through a diffusion dryer. Aerosol number and mass size distributions were measured with a scanning mobility particle sizer (Model SMPS 3080, TSI Inc., Shoreview, MN) coupled with a condensation particle counter (Model 3010, TSI Inc., Shoreview, MN). In this work, both single and multicomponent particles were investigated composed of ODA (≥99%, Fluka, Seelze, Germany), HDA (≥99.0%, Fluka, Seelze, Germany), OL (~99%, Sigma-Aldrich, St. Louis, MO), azelaic acid (AZ) (98%, Sigma-Aldrich, St. Louis, MO), DOS (≥97%, Fluka, Seelze, Germany). The geometric mean diameters and standard deviations of the particles were: OL (93.6 nm, 1.68), ODA (94.5 nm, 1.64), ODA + OL (98.6 nm, 1.59), HDA + OL (108 nm, 1.71), ODA + AZ + DOS (103 nm, 1.66). Typical particle number densities were on the order of 10^7 cm^{-3}. 1-nitrohexane (98%, Sigma-Aldrich, St. Louis, MO) was used to investigate gas phase ionization of nitroalkanes.

Particles were introduced into a concentric glass flow reactor (2.54 cm i.d.) via a glass tube (3 mm i.d.) forming the movable aerosol injector. The flow rate in the reactor was held constant at 0.9 L min^{-1}, such that positioning the aerosol injector from 1 to 51 cm from the end of the flow reactor resulted in reaction times from 0 to 17 s. Ozone was generated from USP Medical Air (UN1002, Airgas East, Williston, VT) or USP Oxygen (UN1072, Airgas East, Williston, VT) below and above 1x10^{-4} atm respectively, by high frequency corona discharge (OL80A/DLS, OzoneLab, Burton, BC, Canada) and quantified spectrophotometrically as described in an earlier report (Zahardis et al., 2006a). Particles entered the PERCI AMS through a 260 μm critical orifice giving a flow rate of 0.5 L min^{-1} and into an aerodynamic lens (Petrucci et al., 2000) to produce a focused particle beam targeted onto a coiled Nichrome filament (LaFranchi and Petrucci, 2006) that could be heated resistively. For all experiments in this study the particle deposition time onto the filament was 2.5 min. After deposition, the filament temperature was ramped from room temperature to 400°C over 10 s and then held at this temperature for 50 s. Anion mass spectra were recorded with a time-of-flight mass spectrometer (R. M. Jordan Inc., Grass Valley, CA) operating in reflectron mode.

Although the emphasis of this work was on investigating the heterogeneous processing of amines in particles, gas phase 1-nitrohexane was studied to better understand the fragmentation of aliphatic nitro compounds by ionization with ~0 eV photoelectrons. In these studies the analyte was introduced into the ionization region of the mass spectrometer with a precision leak valve (model ULV-150, MDC Vacuum Products Corp., Hayward, CA).

3 Results

3.1 PERCI AMS ion profiles of the aliphatic amines, ODA and HDA, in single component particles and mixed particles of ODA (HDA) + DOS

The characteristic PERCI AMS profile for ozonized single-component particles consisting of primary, aliphatic amines was initially established under low and high ozone exposures (Figs. 1a and b, respectively). Both ozonized ODA and HDA (not shown) are characterized by very strong NO_2^- (46 *m/z*) and NO_3^- (62 *m/z*) signals. A NO_2^- signal is evident with and without ozone exposure in single particles of the amines and all mixed particles containing the amines (i.e. OL + ODA (HDA), DOS + ODA (HDA)). However, in all unexposed particles the NO_2^- signal was weak, at about 10% or less than for ozonized particles. The NO_2^- signal is absent when all oxygen is removed from the system (i.e. both O_2 and O_3 are absent), namely when the nebuliser and carrier gases are N_2 or Ar. This implies that the volatilization of primary aliphatic amines in the presence of any oxygen may be a minor channel to NO_2 formation, compared to its direct formation via the oxidation of the amine by ozone. As shown in Fig. 2, the NO_2most likely originates from progressive oxidation by ozone of the amine to the alkylhydroxylamine, then to the nitrosoalkane, and finally to the nitroalkane. This pathway is similar to the mechanism proposed for the ozonation of primary amines to nitro compounds on dry silica gel (Keinan and Mazur, 1977) and in solution (Bachman and Strawn, 1968; Bailey et al., 1972). We do not detect any ions for the proposed nitro alkane end products of ozonized ODA or HDA. The NO_2^- ion can arise from three sources: a) DEA of the nitroalkane, resulting in the formation of the NO_2^- fragment ion; b) thermal decomposition of the nitro alkane (Nazin and Manelis, 1994) either in the flow reactor or c) in the volatilization process producing gas phase NO_2 with subsequent ionization via AEA. To assay the viability of DEA forming NO_2^-, we investigated the ionization of gas-phase 1-nitrohexane at ~0 eV ionization energy (Fig. 3). The base peak corresponding to NO_2^- and a very weak signal arising from the DEA ion corresponding to the loss of hydrogen ($[C_6H_{12}NO_2]^-$, 130 *m/z*) are observed. Similarly, the formation of the NO_2^- fragment with nitromethane (Gilman et al., 1983; Modelli and Venuti, 2001) and several nitrobenzene species (Modelli and Venuti, 2001; LaFranchi and Petrucci, 2004) has been reported with similar ionization energies. Thus it seems likely that nitro alkanes formed from progressive oxidation (Fig. 2) may be the source of NO_2^- that occurs in the ionization process. It should also be noted that there is a weak NO_3^- ion signal in the PERCI spectrum of 1-nitrohexane. This may be an experimental artifact arising from conversion of NO_2 to NO_3 on the metal surfaces (Ozensoy et al., 2005) in the ionization region of the mass spectrometer or from a disproportionation reaction (Reaction 1) (Sekimoto and Takayama, 2007):

$$NO_2^- + NO_2 \rightarrow NO_3^- + NO. \tag{R1}$$

We have evidence that there is decomposition of the particulate nitroalkanes both in the flow reactor and in the volatilization process. The former route to NO_2 formation is supported by the strong NO_2^- signal evident from ozonized particles deposited on the Nichrome filament before heating the wire. Secondly, as shown in Fig. 1, the NO_3^- ion signal increases with ozone exposure, indicating that NO_2 is liberated from the nitroalkanes in the flow reactor at the particles' surface or near surface and then oxidized according to the reaction (Finlayson-Pitts and Pitts Jr., 1999):

$$NO_2 + O_3 \rightarrow NO_3 + O_2. \tag{R2}$$

In the ozonolysis of particle bound amines, the NO_3^- ion signal was strong for all exposures, but increased in intensity with increasing ozone exposure. There are several possible pathways that we believe exist in forming this ion including: a) disproportionation (Reaction 1); b) oxidation of NO_2 by ozone (Reaction 2); and c) conversion of NO_2 to NO_3^- via a surface reaction (Ozensoy et al., 2005) that occurs in the volatilization process. Reaction (2) is likely the most important pathway to NO_3^- due to the concomitant increase in its ion signal intensity with increasing ozone exposure, as well as the very weak ion signal for NO_3 in the gas phase studies that suggest Reaction (1) and surface processes are minor pathways.

There are also medium intensity ion signals in the ozonized ODA and HDA spectra at 125 and 226 *m/z*. These ion signals also increase with ozone exposure. We assign the 125 *m/z* ion signal to NO_3^-•(HNO_3). This ion is the core ion of the series NO_3^-•$(HNO_3)_n(H_2O)_m$, which is the most important negative ion family in the atmospheric at ground level (Heitmann and Arnold, 1983; Perkins and Eisele, 1984). This ion may be formed from the following reaction sequence with the rapid ion-molecule association reaction (Fehsenfeld et al., 1975) being the final step:

$$2NO_2 + H_2O \overset{\text{surface}}{\rightarrow} HONO + HNO_3 \quad \text{(R3a)}$$

$$HNO_3 + H_2O \rightarrow NO_3^- + H_3O^+ \quad \text{(R3b)}$$

$$NO_3^- + HNO_3 \rightarrow NO_3^- HNO_3 \quad \text{(R3c)}$$

Reaction (3a) is the overall stoichiometry of the well-known surface reaction for the hydrolysis of NO_2 (Pitts Jr. et al., 1984; Finlayson-Pitts et al., 2003) that generates both gas phase nitrous acid (HONO) and nitric acid (Finlayson-Pitts et al., 2003). This entire reaction sequence could occur on either the surface of the particle and/or on the surface of the deposited particulate matter on the vaporization coil. The 125 *m/z* ion is observed evolving both before and during the volatilization process, indicating that formation of this ion is not exclusively a result of the thermal vaporization process used in generating the gas phase molecules requisite for ionization in PERCI AMS.

The 226 *m/z* ion does not correspond with any anion cluster in the NO_3^-•$(HNO_3)_n(H_2O)_m$ series, and to the best of our knowledge, it is not a commonly observed ion containing any combination of H, N, and O. This ion is observed not only in the ozonolysis of ODA and HDA, but also for ozonized octylamine (129 u) and lysine (146 u), indicating that it is not an ion *directly* arising from the fragmentation of the amine (or amino acid) or their corresponding nitro compounds. We tentatively assign this ion signal to the cluster NO_2^-•$(HNO_3)_2(H_2O)_3$. Although, to our knowledge, this ion has not been observed, we hypothesize that it could originate from HNO_3•NO_2. This

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species has recently been detected in the attenuated total reflectance FTIR studies of the heterogeneous hydrolysis of NO_2 (Ramazan et al. 2006). A small ion signal at 163 *m/z* is also evident in the PERCI spectrum that becomes more intense with increasing ozone exposure. We tentatively assign this to another member of this proposed ion series, $NO_2^-\bullet(HNO_3)(H_2O)_3$. Another product that may be related to this ion series occurs at 147 *m/z*, which suggests similarity to the 163 *m/z* ion with one less atomic oxygen. Even at high ozone exposures, both the 147 and 163 *m/z* ion signals are relatively weak compared to the four signals discussed previously (i.e. 46, 62, 125, and 226 *m/z*) for the ozonized single-component amine particles. For simplicity, in the remainder of this work we will refer to the 4 strongest ions of the ozonized single-component amine particles as the "characteristic ions of the amine".

Nitrite and nitrate ions were measured in all single-component particles of ODA and HDA and in mixed particles containing the amines and well as DOS as the second component. The DOS + amine PERCI spectrum is relatively simple with three of the ions having been determined to be unique to the ester: the DEA ion ($[DOS\text{-}H]^-$) at 425 *m/z*, and two fragments 295 and 313 *m/z*. These ions probably arise from the fragmentation of the ester linkage (Zahardis et al., 2006b), with 313 *m/z* assigned to $[CH_3(CH_2)_3CH(CH_2CH_3)CH_2OCO(CH_2)_8COO]^-$. The 295 *m/z* ion is tentatively assigned to $[CH_3(CH_2)_3CH(CH_2CH_3)CH_2OCO(CH_2)_6CH{=}CHCO]^-$ or similar dehydration product of the 313 fragment. There was no measureable difference in the PERCI mass spectrum of pure DOS particles upon ozonolysis. The four characteristic ions of the amine were also observed for both ODA and HDA upon ozonolysis of the mixed particles containing DOS. The PERCI mass spectrum of ODA (or HDA) + OL, on the other hand, is far more complex.

3.2 Ozonolysis of ODA (HDA) in mixed particulate matter – overview

DOS and other related high molecular weight esters (Ziemann, 2005; Mochida et al., 2006) employed in studies of heterogeneous ozonolysis are used often as controls because they are not a source of Criegee intermediates (CI). The reactivity of SCI with ODA and HDA was a key feature in the oxidative processing of these mixed particles, especially in the formation of high molecular weight compounds. Ozone concentrations were varied from the same order of magnitude as typical summertime maximum daily concentrations in a suburban-urban troposphere (100–400 ppb i.e. $1-4\times10^{-7}$ atm) (National Research Council, 1991) to very high concentrations: up to $\sim10^{-3}$ atm. Assaying the effects of high ozone concentrations on mixed particles helped in elucidating the mechanisms of oxidation. Secondarily, the products formed under high oxidative stress may be similar to products formed when particulate matter with high amine and lipid content (i.e. meat cooking aerosols) is subjected to both thermal stress and enhanced ozone levels associated with the urban troposphere.

For conciseness, the ensuing discussion places emphasis on comparing the low ozone exposure regime (which we define as $10^{-6}-10^{-7}$ atm ozone for ~17 s) to the very high ozone exposure regime ($\geq10^{-3}$ atm for ~17 s).

3.3 Ozonolysis of ODA (HDA) + OL in mixed particles: products assignments for low ozone exposure

Figures 4a, b compare PERCI mass spectra for the ozonolysis of mixed ODA/OL particles at 3×10^{-7} atm and 2×10^{-3} atm ozone, respectively, for a 17 s reaction time. Of the four expected lower molecular weight products of the heterogeneous ozonolysis of OL (i.e., azelaic acid (AZ, 188 u), 9-oxononanoic acid (OX, 172 u), nonanoic acid (NA, 158 u), and nonanal (NL, 142 u) (Zahardis and Petrucci, 2007)), only AZ (187 *m/z*) is observed for the mixed particles (ODA (HDA) + OL), at very low exposure. On the other hand, all 4 characteristic ions expected from reaction of the aliphatic amine (46, 62, 125, and 226 *m/z*), as well as the minor ions at 147 and 163 *m/z* are observed.

At ozone exposures of $\sim3\times10^{-7}$ atm (17 s) and higher in the ODA + OL system, we also observe ions at 422 and 438 *m/z*. The 438 *m/z* ion is assigned to the amide that may be formed by several pathways, including reaction of the SCI-I (c.f. Fig. 2) with ODA. The 422 *m/z* ion could arise from a 423 u product that is either an amide or an imine (i.e. Schiff base). The amide could be formed from ODA

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and OX, with the amine reacting at the carboxyl position. The imine (i.e. Schiff base), 9-(octadecylimino)nonanoic acid, could be a product of the reaction of ODA with the aldehyde functionality of OX. This ion is nominally one mass unit lower than the mass of the proposed ion indicating DEA ionization via the loss of hydrogen. These assignments are supported by ion signals measured at 394 and 410 *m/z* in the HDA + OL mixed particles (p_{O3}=3×10^{-7} atm and 17 s reaction time). These higher molecular weight signals are assigned to the amides and imine corresponding with reaction of HDA with OX and SCI-I respectively. These ions are not observed at lower concentrations of ozone in the ODA (HDA) + OL reaction system. These ion signals are also not observed under any conditions of ozone exposure for ODA or HDA in DOS. It should be noted that we do not observe any DEA ion for the amides that could be the product of the reaction of the 158 u SCI (SCI-2, i.e. $OOCH(CH_2)_7CH_3$) with ODA or HDA. These amides would have an alkyl end, unlike the amides arising from the reaction of SCI-1 which have a carboxyl group functionality. It is likely that SCI-2 does form amides with these amines, but they are not ionized to any significant extent with ~0 eV electrons, as is the case with all organic acids (LaFranchi et al., 2004; Zahardis et al., 2005; LaFranchi and Petrucci, 2006; Zahardis et al., 2006a) investigated to date. The high molecular weight, nitrogen-containing products measured and their corresponding assignments are summarized in Table 1.

3.4 Ozonolysis of ODA (HDA) + OL in mixed particles: products assignments for high ozone exposure

The mass spectrum of products arising from heterogeneous reaction ODA(HDA) + OL aerosols with ~2×10^{-3} atm ozone at ~17 s reaction time (Fig. 4b) shows the four characteristic ions of the aliphatic amine (i.e. 46, 62, 125, and 226 *m/z*) in addition to two distinct regions of high molecular weight products, mainly the DEA ions of secondary and tertiary amides formed via the secondary reactions of ozonolysis. The four classical products of OL ozonolysis are also evident in both the ODA and HDA mixed particles. Interestingly, the OL molecular ion at 281 *m/z* is one of the strongest ion sig-

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nals in the PERCI mass spectrum for the ozonolysis of ODA + OL aerosols (Fig. 4), but only a very weak signal in the HDA + OL system at this same exposure (not shown). Under identical exposure conditions, the OL molecular ion was not observed in the reaction of pure OL particles. Moreover, for the pure OL particles, no OL molecular ion was observed for any ozone concentration above 1×10^{-4} atm ozone for ~17 s reaction time. We believe these unanticipated effects (i.e. the retention of OL in the ODA + OL reaction system at this very high ozone exposure) originate from surface or near surface reactions that produce high molecular weight secondary and tertiary amides. These surface active species, in turn, may impede the diffusion of ozone into the particle and limit the diffusion of OL to the surface, thereby effectively shutting down the ozonolysis of OL.

3.5 A mechanistic account for the formation of the observed products in the ozonized mixed particles

A detailed account of the heterogeneous ozonolysis of OL has recently been published (Zahardis and Petrucci, 2007) and many mechanistic depictions are available in the literature (Katrib et al., 2004; Hung et al., 2005; Zahardis et al., 2005; Ziemann, 2005; Reynolds et al., 2006). The three main steps of ozonolysis of oleic acid are in accord with established solution phase chemistry (Bailey, 1978):

Step 1) formation of the primary ozonide (POZ, or a 1, 2, 3-trioxolane)

Step 2) decomposition of the POZ to aldehydes and excited Criegee intermediates (ECI), which in solution rapidly stabilize to SCI

Step 3) recombination of the SCI and aldehyde to form secondary ozonides (SOZ) (or undergo intermolecular reactions to form diperoxides)

There exists considerable debate concerning the formation of AZ and NA and their relationship with SCI-1 and SCI-2 (Zahardis and Petrucci, 2007). It has been suggested that these two acids are formed from isomerization of SCI-1 and SCI-2 (i.e. $OOCH(CH_2)_7CO_2H$ and $OOCH(CH_2)_7CH_3$) (Hearn and Smith, 2004; Hung et al., 2005; Zahardis et al., 2005; Ziemann, 2005) or, conversely, form as decomposition products of the SOZ and other peroxides as higher generation reaction products (Martin, 2006b; Martin, 2006a). Recent mass spectral evidence (Reynolds et al., 2006) suggests that fragmentation occurring in the ionization process of high molecular weight peroxides may also contribute to the evolution of ions corresponding to these acids. A more extensive discussion of the formation of these acids as well and other mechanistic features of this reaction system are beyond the scope of this report and have been covered elsewhere (Zahardis and Petrucci, 2007).

The amide 9-(octadecylamino)-9-oxononanoic acid (439 u, 438 *m/z*) may be formed by several different routes in the ozonolysis of ODA + OL. Route 1 is the well-established route via acylation of an amine by a carboxylic acid (i.e. AZ) (Satchell, 1963), which we believe to be a minor pathway in the formation of amides in these heterogeneous reaction systems. Route 2 involves reaction of the amine (ODA) with SCI-1 (Fig. 5a), while Route 3 may result in amide formation via reaction of ODA with an SOZ (Fig. 5b). Similar routes exist for the formation of 9-(hexadecylamino)-9-oxononanoic acid (411 u, 410 *m/z*) in the HDA + OL reaction system.

We tested the relative importance of Routes 2 and 3 by preparing mixed particles with a very high concentration of AZ. These mixed particles contained the inert matrix DOS, which like other esters does not undergo ozonolysis or react with SCI (Ziemann, 2005; Mochida et al., 2006). Figure 6 compares the evolution of the 438 *m/z* amide between the AZ + ODA + DOS and ODA + OL heterogeneous reaction systems, at four ozone concentrations. The 438 *m/z* ion was either not observed or was a very weak signal in the AZ + ODA + DOS mixed particles under all exposure conditions. Further, no other ion signals corresponding to amides were observed in the AZ + ODA + DOS heterogeneous reaction system. On the other hand, the 438 *m/z* amide was produced in significant amounts in the ODA + OL reaction system (Fig. 6) and was directly proportional to the ion signal for AZ generated in situ to the ODA + OL particle. The direct proportionality of amide formation with AZ does not contradict the aforementioned result because the AZ signal we measure is directly proportional to the in situ generated SCI-1 and likely directly proportional as well with SOZ in the system that can decompose to the acid. Our results indicate it is the reactivity of these chemical classes (i.e. SCI and SOZ) with the amines that constitute the main routes to amides; however, with the extant data there is no way to estimate the relative importance of Route 2 vs. 3.

3.6 The formation of a solid or viscous surface layer

The OL ion signal was measured for three types of ozonized particles as a function of ozone exposure: (neat) OL, ODA + OL, and HDA + OL (Fig. 7). The OL ion signal in neat particles and mixed particles of HDA + OL follows an exponential decay at low ozone exposures. Neither of these particles shows a measurable OL signal at ozone exposures above 1×10^{-4} atm at 17 s reaction time. In the ODA + OL reaction system, on the other hand, OL decays exponentially initially up to an ozone exposure of 1×10^{-4} atm but then re-emerges at very high exposures ($\geq 6\times10^{-4}$ atm for 17 s reaction). This suggests that at a critical level of ozone exposure, the particles develop a solid or highly viscous liquid surface layer that impedes the diffusion of ozone into the particle. Similar effects have been observed in the formation of solid surface layers with ozonized myristic acid + OL particles (Nash et al., 2006). Figure 8 compares the PERCI ion signal of OL (281 *m/z*) to the ion signal of 5 high molecular weight imine and amide products (422, 438, 576, 592 and 608 *m/z*) and the integrated ion intensity for all observed amide/imine signals. The ion intensity of the 438 *m/z* amide increases rapidly for ozone exposures in the range 0 to 1×10^{-4} atm and 17 s reaction time. Furthermore, no appreciable increase in intensity is measured at higher exposures. In comparison, the 422 *m/z* amide/imine and the three high molecular weight tertiary amides show less rapid initial increase in their ion intensity with a linear, generally monotonic, increase in intensity at exposures above 1×10^{-4} atm O_3. The total amide/imine ion intensity rapidly rises for a 17 s reaction with $0–1\times10^{-4}$ atm O_3. At higher exposures, a linear, monotonic increase is observed, with the exception of the 1×10^{-3} atm O_3 exposure, where there is a slight decrease in the PERCI ion intensity. From these data, we cannot definitively assign any particular imine or amide with the formation of a solid or viscous liquid layer that impedes the diffusion of ozone into the particle, although it appears that the best correlation is between the total amide/imine content and the formation of this layer.

4 Conclusions and implications

The experiments described in this work have lead to several significant observations for the ozonolysis of particle bound amines.

1. Our observation of a strong ion signal corresponding to nitrogen dioxide indicates nitro alkanes are generated from primary aliphatic particulate amines by the mechanism of progressive oxidation (Bachman and Strawn, 1968; Bailey et al., 1972; Keinan and Mazur, 1977). This is in accord with the ozonolysis of amines in solution (Bachman and Strawn, 1968; Bailey et al., 1972) and on dried surfaces (Keinan and Mazur, 1977) rather than in the gas phase (Tuazon et al., 1994; Angelino et al., 2001; Murphy et al., 2007), where large yields of aldehydes would be anticipated (Tuazon et al., 1994). We do not observe any aldehyde or other oxygenate signal in the ozonolysis of single component particles of amines under any conditions of ozone exposure. This probably stems from the stabilization of either the amine oxide or alkylhydroxylamine (Fig. 2) early in the reaction sequence in the ozonolysis of the particulate amines. Stabilization would favor the formation of the nitrosamine, which is subsequently oxidized to the nitro alkane. This is quite different than in the gas phase, where the excited amine oxide or alkylhydroxylamine intermediate fragments (Tuazon et al., 1994), leading to a host of products including nitro alkanes, aldehydes, and imines.

2. The ozonolysis of particles of primary, aliphatic amines may represent a source

of NO_2, NO_3 and nitric acid ion clusters, even at ozone concentrations that correspond to a polluted suburban-urban troposphere (National Research Council, 1991). The experimental data reported herein suggests that progressive oxidation of amines leads to NO_2 formation, with subsequent formation NO_3 through progressive oxidation (as described above) and finally nitric acid ion clusters. This may help explain, in part, the mechanism by which organic nitrogen in fog water and aerosols acts as a source of NO_x and NO_3 during exposure to ozone (Zhang and Anastasio, 2003). Future emphasis will be placed on quantification of NO_2, NO_3, and the nitric acid ion clusters via PERCI for the ozonolysis of a wider array of particle bound organic species that contain amine nitrogen. This is inherently challenging because may of the anticipated products (i.e. NO_2 and NO_3) do not have well-established capture cross-sections for very low energy photoelectrons. We will also investigate the effects of relative humidity on the formation of nitric acid ion clusters.

The experiments described in this work have lead to several significant observations in the heterogeneous ozonolysis of mixed particles containing amines:

1. Secondary and tertiary amides and possibly imines are potentially important reaction products of the heterogeneous ozonolysis of aliphatic primary amines in particles, when SCI can be generated in situ to these mediums. These products are evident even at relatively low ozone exposures for relatively short reaction times. This implies that in regions where there is a high atmospheric input of amines (i.e. near animal husbandry operations, Schade and Crutzen, 1995), there may be an enhanced incorporation of these nitrogen-containing species into particles. CI have been shown to form and react near or on the surface of ozonized OL particles (Moise and Rudich, 2002; Smith et al., 2002; Katrib et al., 2004; Hearn et al., 2005). When gas-phase amines partition to the surface of an ozonized particle that contains SCI and/or SOZ, they may react via Routes 2 and/or 3 to form the lower volatility amides. This is evidenced by our observation of these high

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molecular weight products even at low ozone exposures (c.f. Fig. 1a). These reactions represent new pathways by which amine nitrogen may be converted to lower volatility particle bound nitrogen. They may also help explain the mechanism of forming nitrogen enriched HULIS (Likens and Galloway, 1983; Decesari et al., 2006) and may be important in the atmospheric aging of organic aerosols. Moreover, amides, compared to other acylation products such as esters, are relatively stable to hydrolysis (Satchell, 1963), resulting in the potentially long atmospheric lifetime of these nitrogen containing species in particles. The viability of gas-to-particle conversions of amine nitrogen via these mechanisms will be the focal point of upcoming environmental chamber experiments in our laboratory where we will examine the effects of prolonged ozone exposure (hours to days) of more common atmospheric amines (i.e. ethyl amines) in the presence of unsaturated acids at ozone levels in accord with a polluted suburban-urban troposphere.

2. Although amide production is in accord with well-established solution acylation reactions (i.e., between the carboxylic acids and the amine, Satchell, 1963), our data implies that the major pathway(s) in ozonized particles of ODA (HDA) + OL is through the reaction of SCI and/or SOZ with the amine. This may have ramifications to source apportionment where it has been suggested that amides can be utilized as molecular markers (Simoneit et al., 2003) for biomass burning events, since they can be generated by standard (i.e. Route 1) acylation under pyrolysis. Although we agree with the importance of this route of amide formation under biomass burning conditions, we need to establish the viability of the role of secondary chemistry of ozonolysis in sequestering amine nitrogen into particulate matter via amide formation (i.e. Routes 2 and 3). These routes, if important competing pathways to amide formation through acylation would indicate that amides may also be molecular markers for regions that have concurrent high levels of ozone and amine input, i.e. animal husbandry operations near polluted suburban-urban environments.

3. There is evidence of solid surface or highly viscous liquid layer formation in ODA + OL at high ozone exposures. This may impede the diffusion of ozone into the particle causing retention of OL at these very high exposures, where it would be totally consumed in single component particles of OL. This observation and similar ones by others (Nash et al., 2006) in fatty acid rich particulate, along with the retention of OL even at high exposures, may help elucidate the disparity that exists between the lifetime of OL measured in the field vs. in the laboratory (Zahardis and Petrucci, 2007). The formation of high molecular weight amides is likely to occur in meat-cooking aerosols that are rich in both fatty acids and amines and that are formed under conditions of high temperature (facilitating Route 1 amide formation). Amide formation is especially significant when generated in a polluted, ozone rich troposphere (facilitating amide formation via Routes 2 and 3). The prolonged lifetime of OL in real meat cooking aerosols vs. single-component particulate OL matter has also been demonstrated experimentally (Hearn and Smith 2006). Although we only observe the solid surface or highly viscous liquid layer formation in the OL + ODA reaction system under conditions of very high ozone exposure (1×10^{-4} atm O_3, 17 s reaction time), we need to investigate the effects of prolonged exposure of particles to lower levels of ozone ($\sim 10^{-7}$ atm O_3) with experiments in environmental chambers. Although not explored in this work, other condensed phase thermo-chemical effects that may cause a prolonged lifetime of OL and other unsaturated components of real atmospheric aerosols, such as gel or semisolid formation, or Ostwald ripening in amide enriched aerosols needs to be explored as well.

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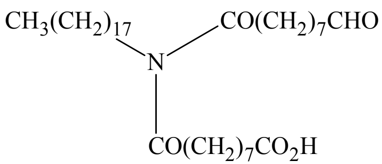
Table 1. High molecular weight, nitrogen containing products formed in the heterogeneous ozonolysis of mixed ODA + OL particles and their corresponding assignments. The corresponding ions, with masses 28 u lower, were observed also in the HDA+OL system.

Compound	Chemical Product	Comments
1	$CH_3(CH_2)_{17}NHCO(CH_2)_7CHO$	422 m/z, Secondary amide, ODA + OX -H_2O
2	$CH_3(CH_2)_{17}N{=}CH(CH_2)_7CO_2H$	422 m/z, imine, ODA + OX -H_2O
3	$CH_3(CH_2)_{17}NHCO(CH_2)_7CO_2H$	438 m/z, secondary amide, ODA + SCI-1 -H_2O
4	$CH_3(CH_2)_{17}N(CO(CH_2)_7CHO)_2$	576 m/z, tertiary amide, ODA + 2 OX -2 H_2O
5		592 m/z tertiary amide, ODA + OX + SCI-1 - 2 H_2O
6	$CH_3(CH_2)_{17}N(CO(CH_2)_7CO_2H)_2$	608 m/z tertiary amide, ODA + 2 SCI-1 - 2 H_2O

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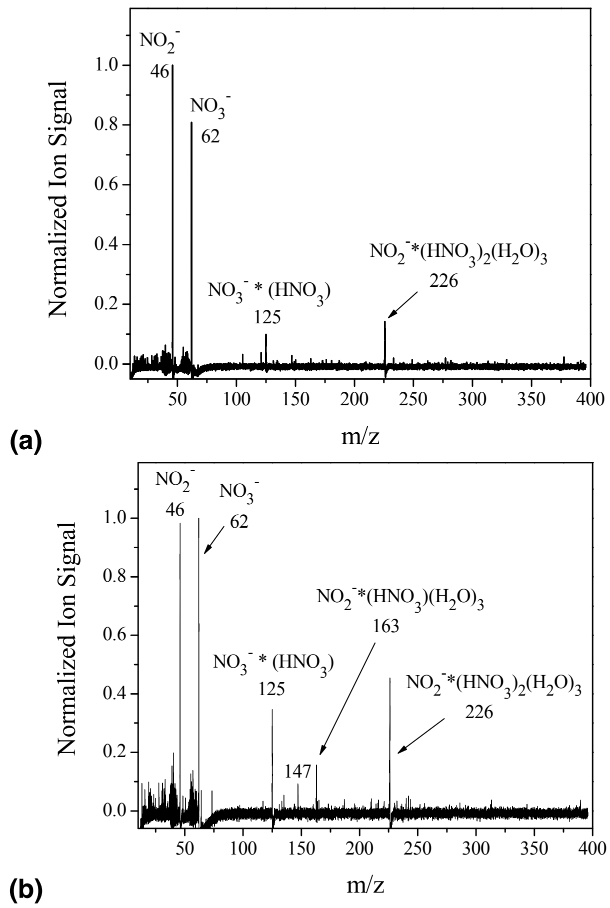

Fig. 1. PERCI mass spectrum of ozonized single component particles of ODA at p_{O3} = **(a)** 1×10^{-4} atm and **(b)** 2×10^{-4} atm. Reaction time was 5 s.

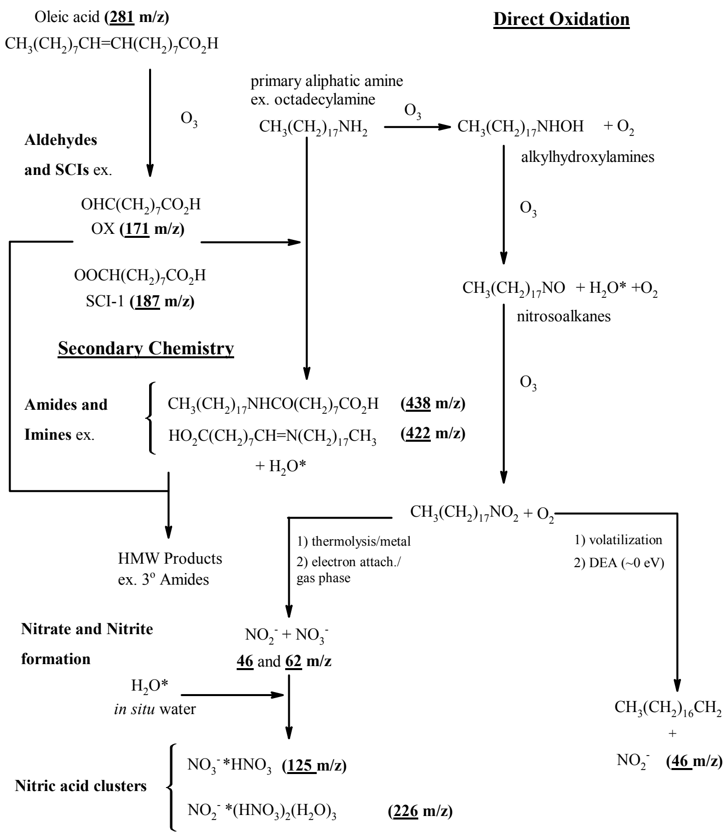

Fig. 2. Pathways of direct oxidation and secondary reactivity with ozonized amines (ODA shown as an example). The pathway labeled Direct Oxidation occurs with both single component particulate amines and in mixed particles with the amine + OL. All products observed are underlined. The direct oxidation products are identical with ozonized HDA. The amides and imines that form in the HDA + OL mixed particles are similar in structure to those indicated, except 28 u lower in mass.

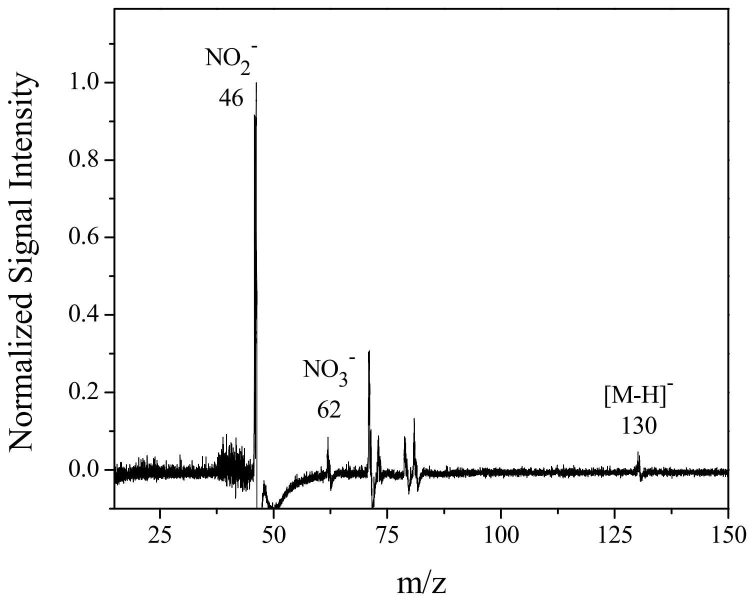

Fig. 3. PERCI mass spectrum of 1-nitrohexane introduced into the PERCI AMS as a gas ($p=2\times10^{-5}$ atm). Photoelectron energy was ~0 eV.

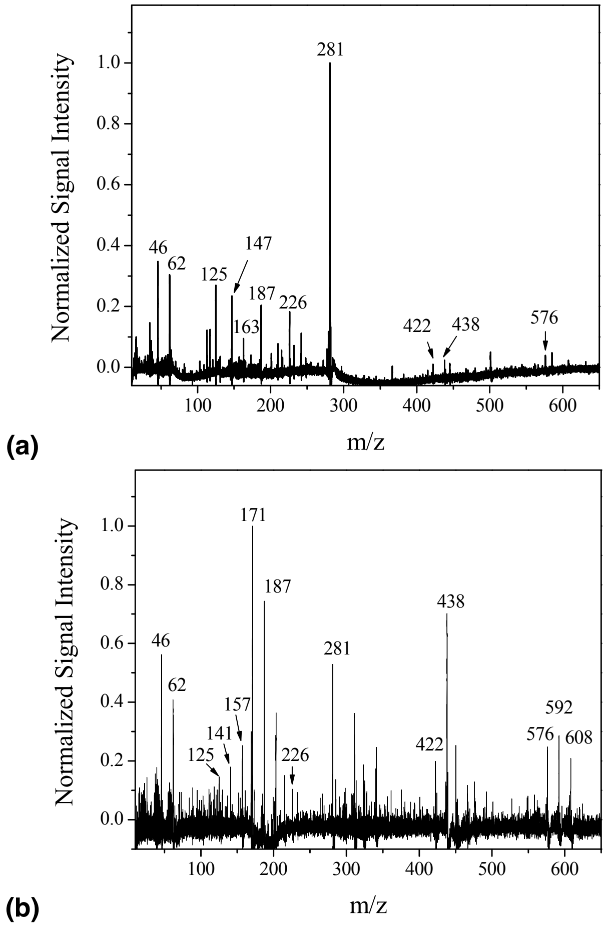

Fig. 4. PERCI mass spectrum of ozonized mixed particles of ODA + OL at p_{O3} = **(a)** 3×10^{-7} atm and **(b)** 2×10^{-3} atm. Reaction time was 17 s. Mole fractions, χ, were χ_{ODA}=0.41 and χ_{OL}=0.59.

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Ozonolysis of primary aliphatic amines in fine particles

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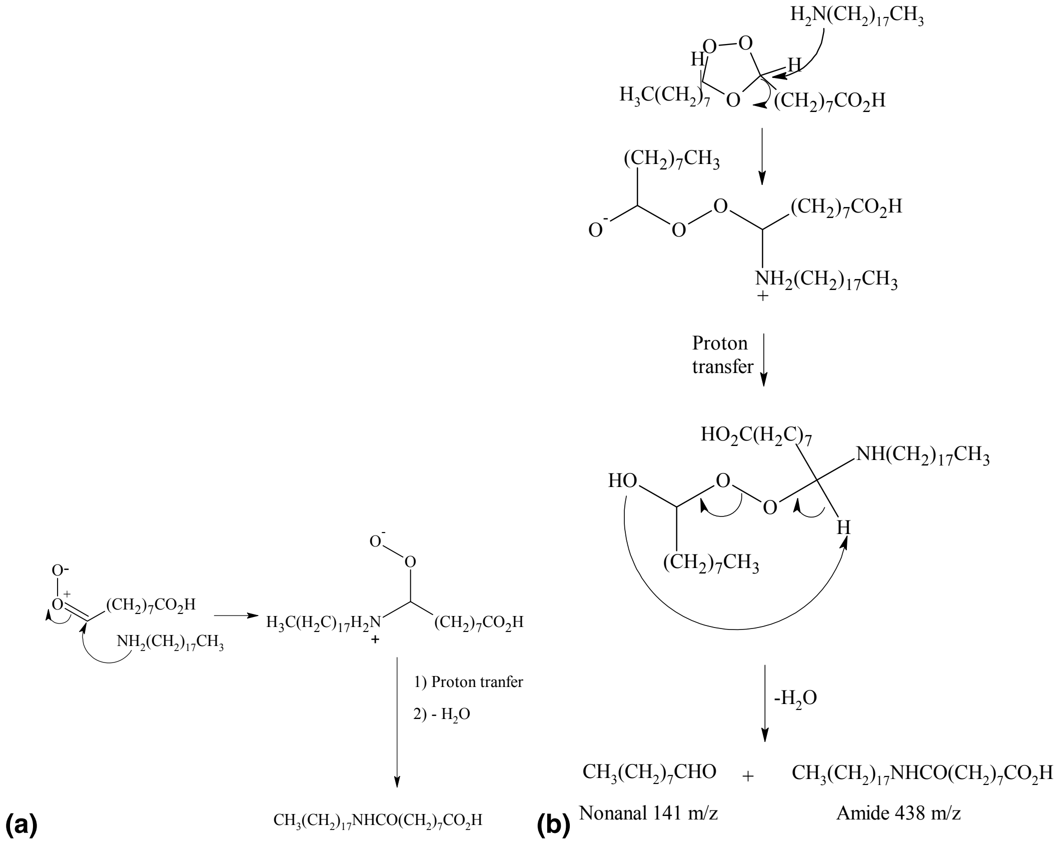

Fig. 5. Proposed mechanisms for observed amide formation via reactions of amines with products of ozonolysis of OL. Amide formation via reaction of **(a)** ODA with an SCI (shown SCI-1) and **(b)** ODA and an SOZ. Similar reactions for HDA are discussed in text.

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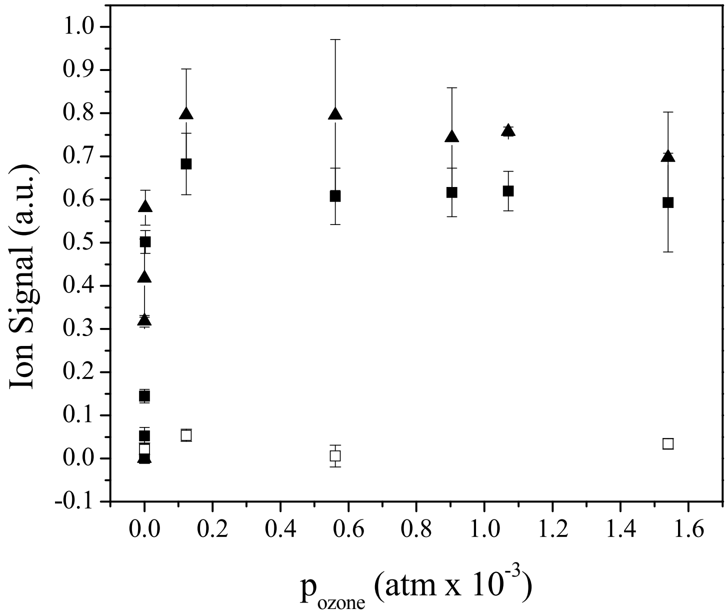

Fig. 6. Formation of a (■) secondary amide (438 *m/z*) and (▲) SCI-I (187 *m/z*) in ODA + OL mixed particles (χ_{OL}=0.59, χ_{ODA}= 0.41) compared to formation of (□) secondary amide (438 *m/z*) in AZ + ODA + DOS mixed particles (χ_{AZ}=0.22, χ_{ODA}=0.24, χ_{DOS}=0.54) with no possible concurrent formation of SCI-I in particle. Error bars indicate one standard deviation.

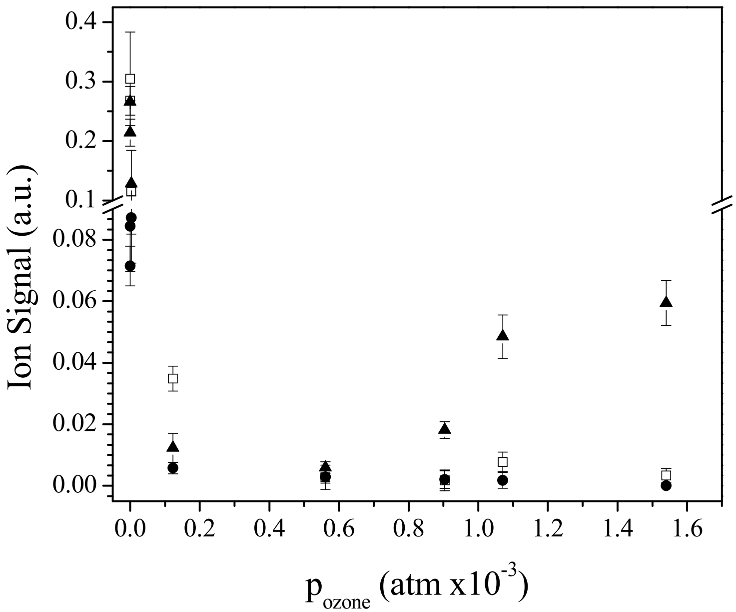

Fig. 7. Comparison of OL decay for three particle types: (•) neat OL particles, (▲) ODA + OL mixed particles, and (□) HDA + OL mixed particles. Mole fractions, χ, were $\chi_{ODA/HDA}$=0.41 and χ_{OL}=0.59.

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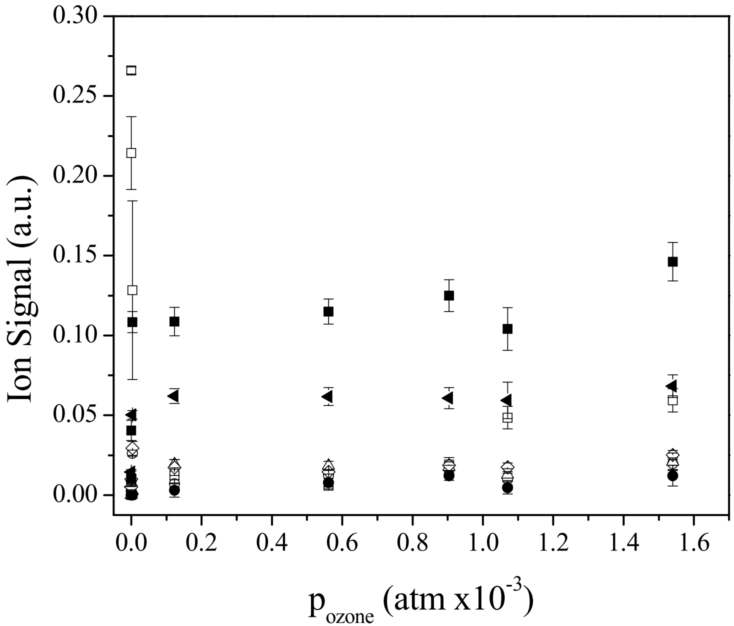

Fig. 8. OL decay and the formation of amides and imine in ozonized mixed particles of ODA/OL: (■) integrated ion intensity for all amides and imines (Compounds 1–6) measured; (□) OL; (◂) 438 *m/z* secondary amide; (O) 576 *m/z* tertiary amide; (Δ) 592 *m/z* tertiary amide; (•) 608 *m/z* amide; and (◇) secondary amide or imine at 422 *m/z*. Mole fractions, χ, were χ_{ODA}=0.41 and χ_{OL}=0.59.

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